United States Environmental Protection Agency

# Characterization and Development of Measurement Methods for Ambient Nitrogen Dioxide ($NO_2$)

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# Research Questions and Motivation:

United States Environmental Protection Agency

- How do direct, optical measurements of $NO_2$ compare with the Federal Reference Method and photolytic conversion techniques?

- What is the optimum method for calibration and span/zero checks for each type of monitor (Gas Phase Titration of NO vs bottled $NO_2$)?

- EPA's ORD interest in accurate $NO_2$ measurements supports:
    - Reference and equivalent method determinations and evaluations
    - EPA's monitoring networks
    - Ground-based satellite validation work with NASA

# Outline

I. $NO_2$ sources, trends, and regulations
II. Gas-phase chemiluminescence measurement methods:
    a. Federal Reference Method
    b. Photolytic conversion
III. Direct, optical techniques:
    a. Cavity ringdown spectroscopy (CRDS)
    b. Cavity attenuated phase shift (CAPS)
IV. Results from DISCOVER-AQ Campaign
V. Preliminary Results from RTP, NC

# Atmospheric nitrogen families

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$NO_x = NO + NO_2$ **"nitrogen oxides"**

$NO_y = NO_x + HNO_3 + \ldots$ **"total reactive nitrogen"**
$HONO + RONO_2 + RO_2NO_2 + NO_3 + N_2O_5 + NO_3^-(p)$

$NO_z = NO_y - NO_x$ **"reacted oxides of nitrogen"**

- **$NO_2$** serves as the **indicator species** for the family of the oxides of nitrogen.

# Current $NO_2$ Regulations

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• Clean Air Act requires EPA to set National Ambient Air Quality Standards (NAAQS) for criteria pollutants:

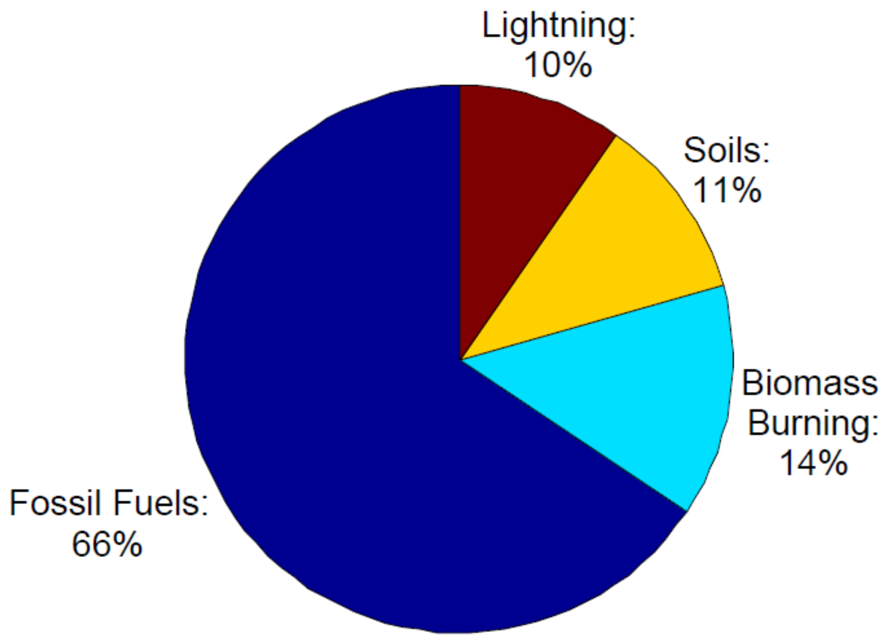
| $NO_2$ Primary Standards | | |
|---|---|---|
| *level* | *averaging time* | *year implemented* |
| 53 ppb | Annual | 1971 |
| 100 ppb* | 1 hr | 2010 |

* The new monitoring locations for the Jan 2010 primary standard will be sited in near roadway locations to capture areas of maximum concentration. (http://epa.gov/ttn/amtic/nearroad.html)

* Continuous monitors capable of hourly data are now necessary.

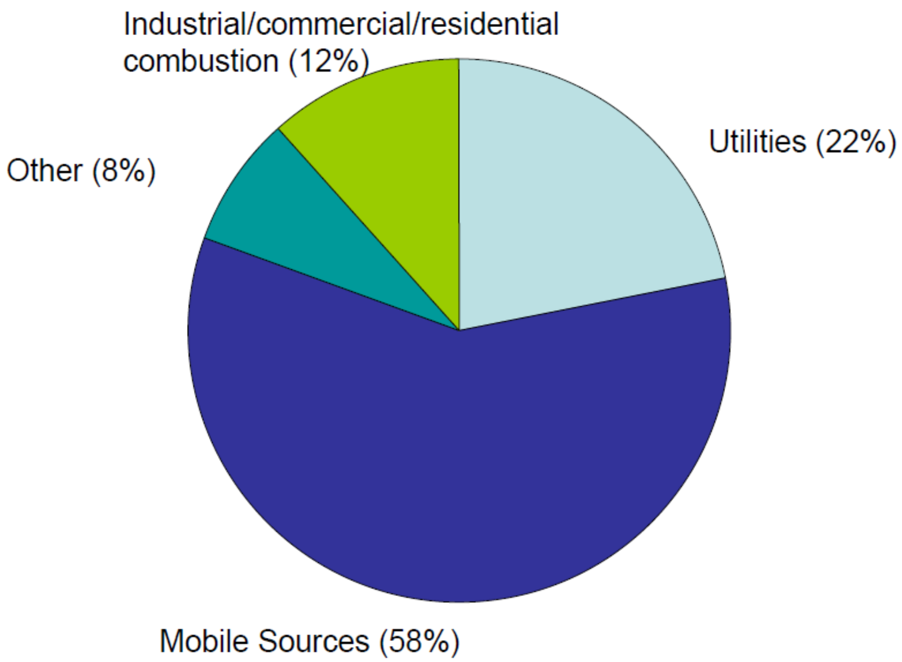
# What are the sources of $NO_x$?

Global (natural and anthropogenic):




Based on IPCC (2001) data

anthropogenic (US):




Based on 2002 National Emissions Inventory Data

- Primarily emitted as NO
- Emissions reductions aimed at mobile and point sources

# Emissions of $NO_2$ are declining

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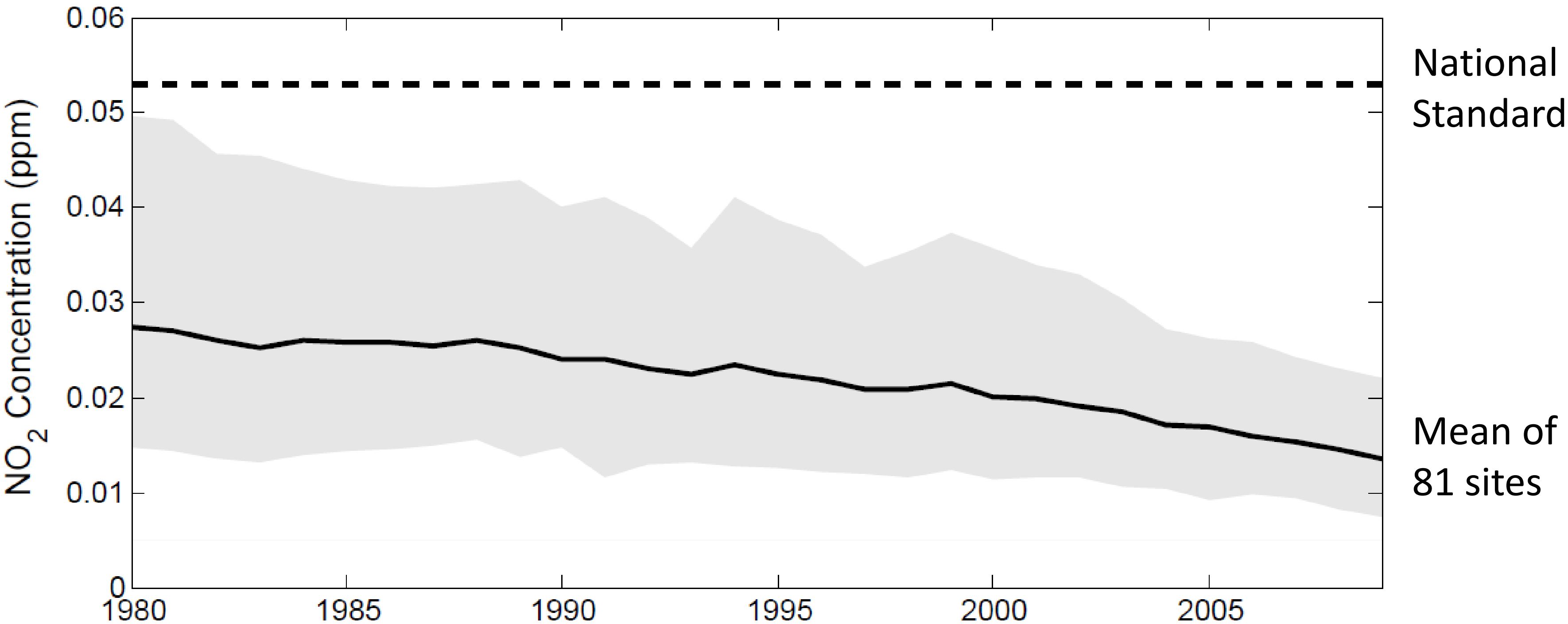



- 48% decrease in the national average.
- Achieved by reducing $NO_x$ for $O_3$ purposes (mobile and point source regulations).



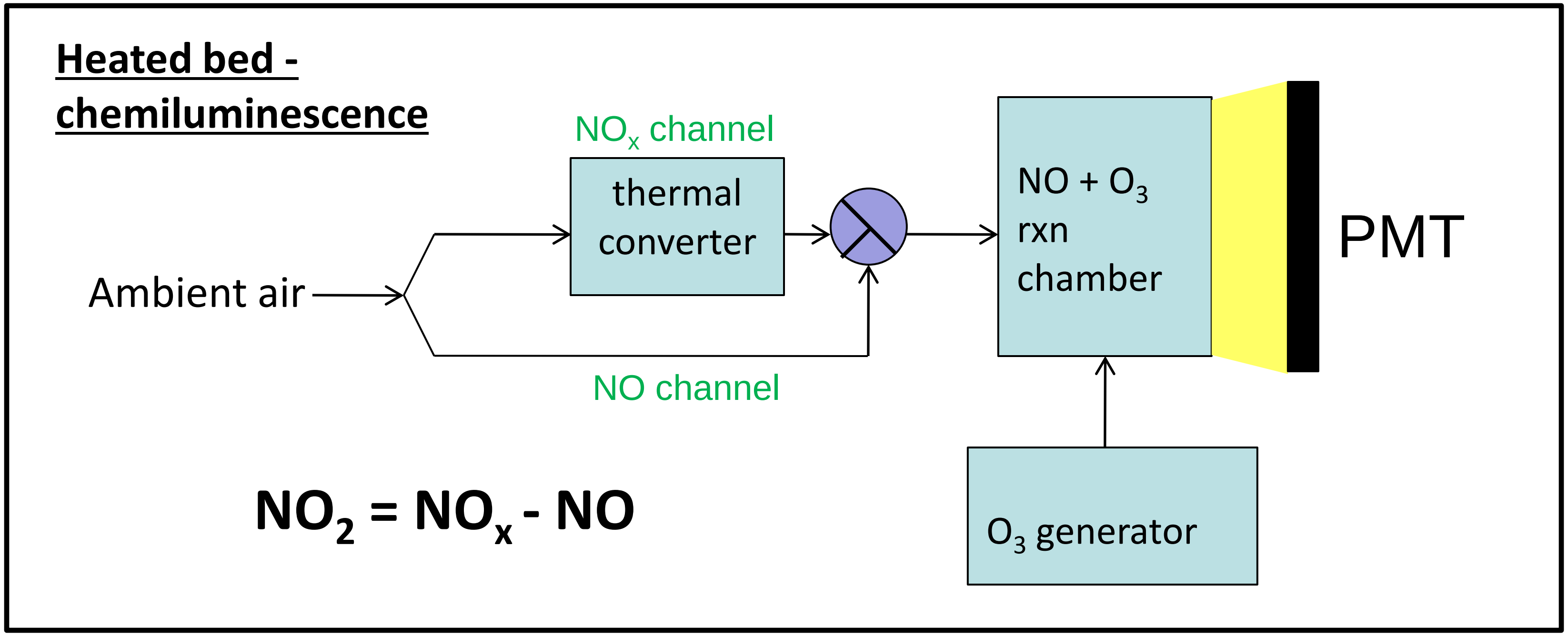
Data from EPA's Air Quality System (AQS)

# How is $NO_2$ (currently) measured?

- Federal (Automated) Reference Method (40 CFR, Part 50, Appendix F):

  -**Gas-phase chemiluminescence**

  -Indirectly measure $NO_2$ by conversion to NO, then NO is detected by chemiluminescence ($NO + O_3 \rightarrow NO_2^*$, $NO_2^*$ = excited state);




-Advantage→ in use since the 1970s (long term record)

-Disadvantages → non-specific; indirect

# Method has possible interferences

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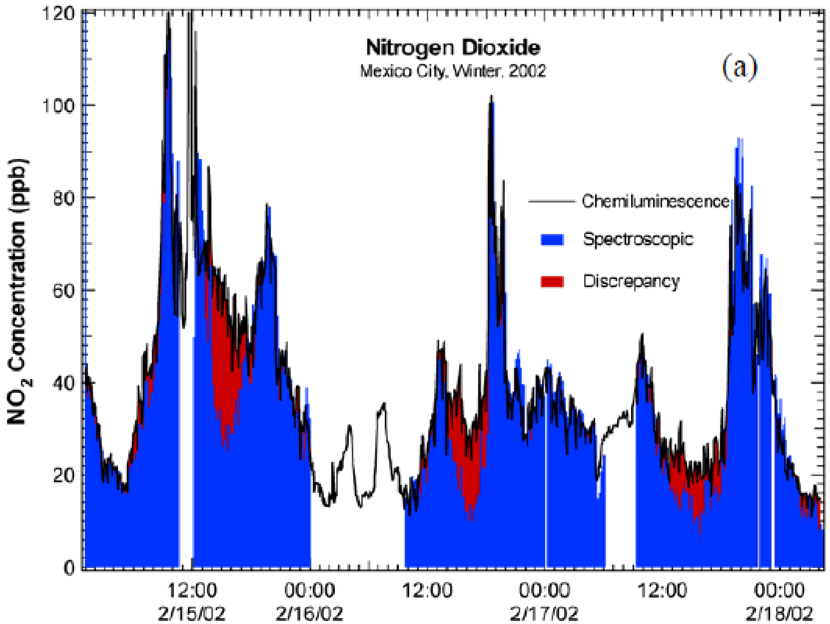
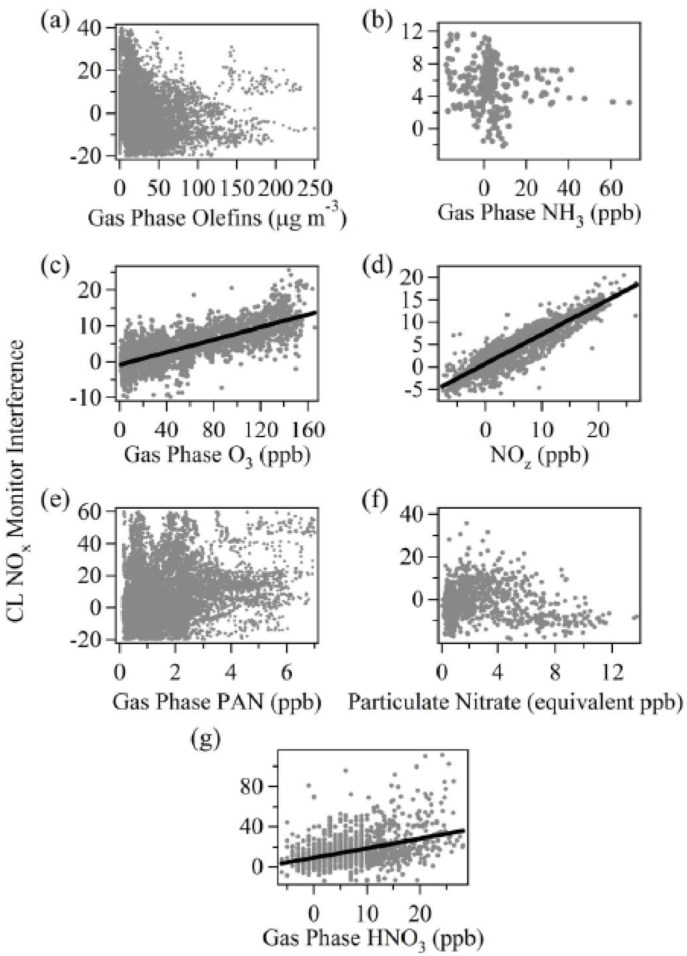
- Non-specific to $NO_2$ → heated metal catalysts known to convert other $NO_y$ species to NO.



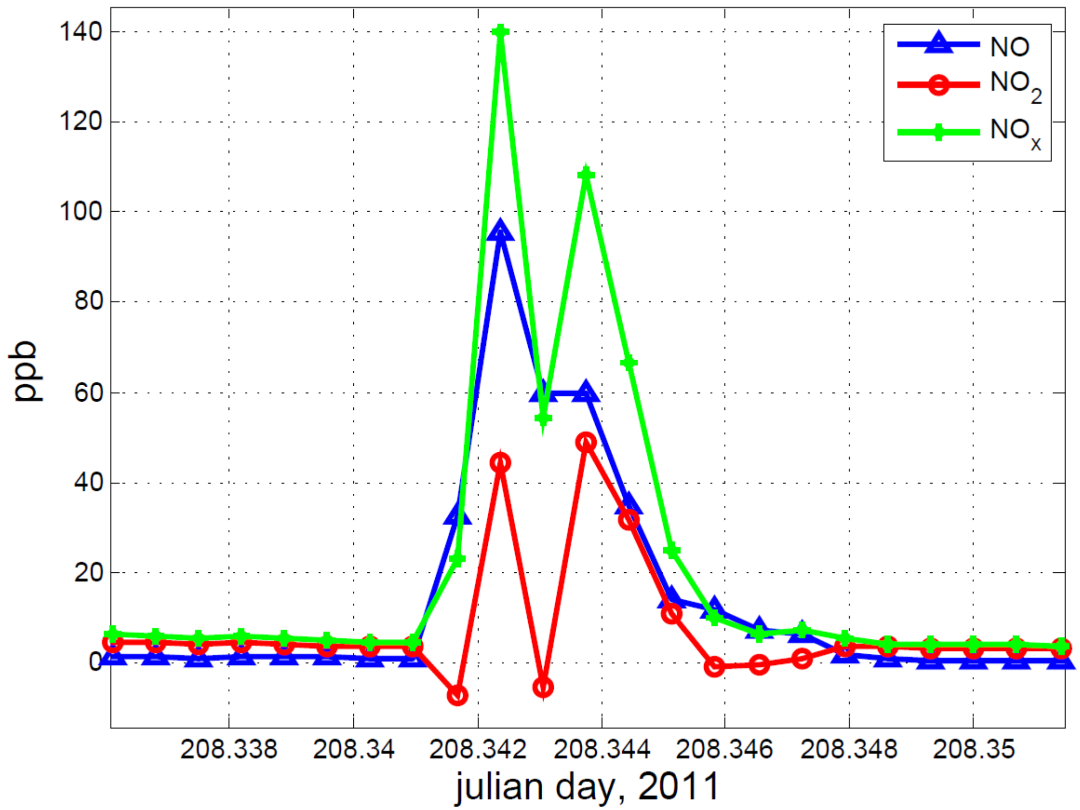

- Considered an upper limit measurement of $NO_2$.



Dunlea et al. ACP (2007)

# Method has possible interferences

• NO spikes → The indirect determination requires a slowly changing $NO_x$ distribution. Otherwise, negative spikes of $NO_2$ are possible:



# Alternative Technique: Photolytic-chemiluminescence

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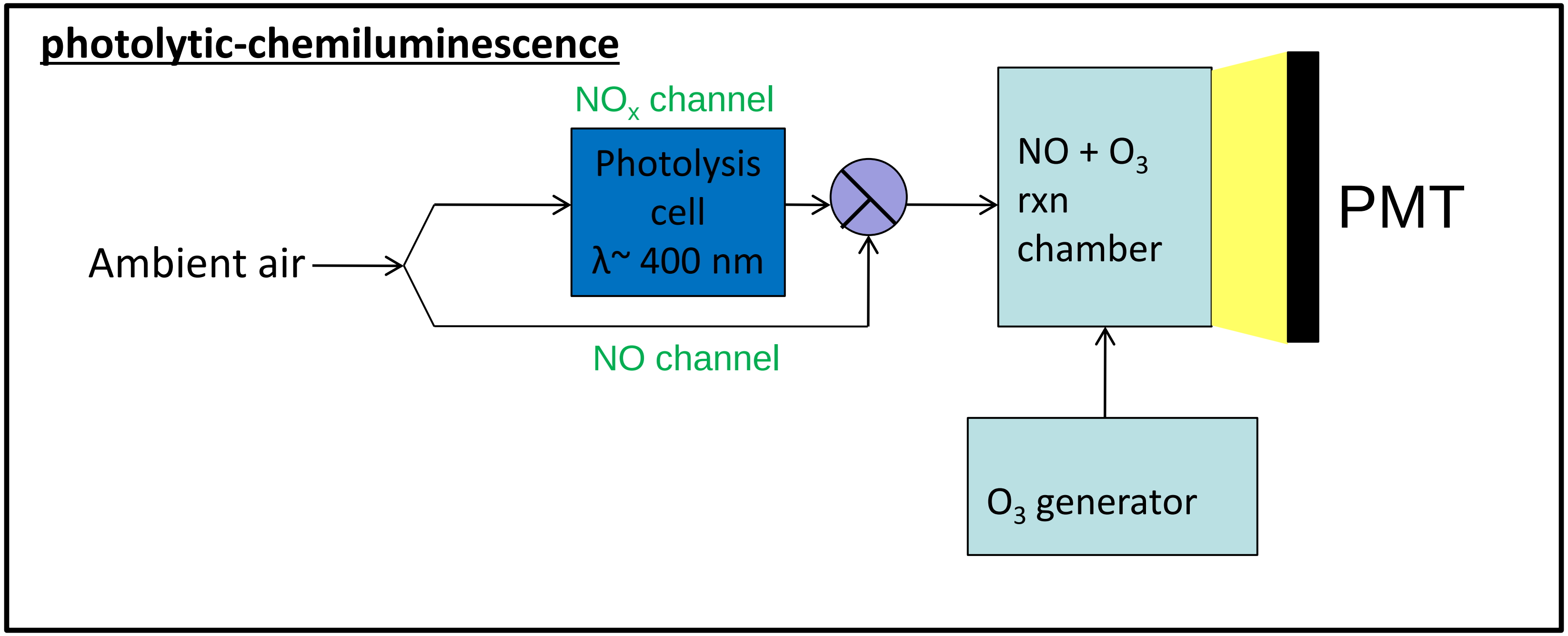
• Replace the metal bed reducer with a photolysis cell to photolyze $NO_2$ to NO ($NO_2$ + *hv* → **NO** + O).

-Use high-power light sources to maximize conversion to NO.




- Advantage → more specific to $NO_2$
- Disadvantages → non-unity conversion efficiency; still indirect

# UV/Vis Spectroscopy of $NO_2$

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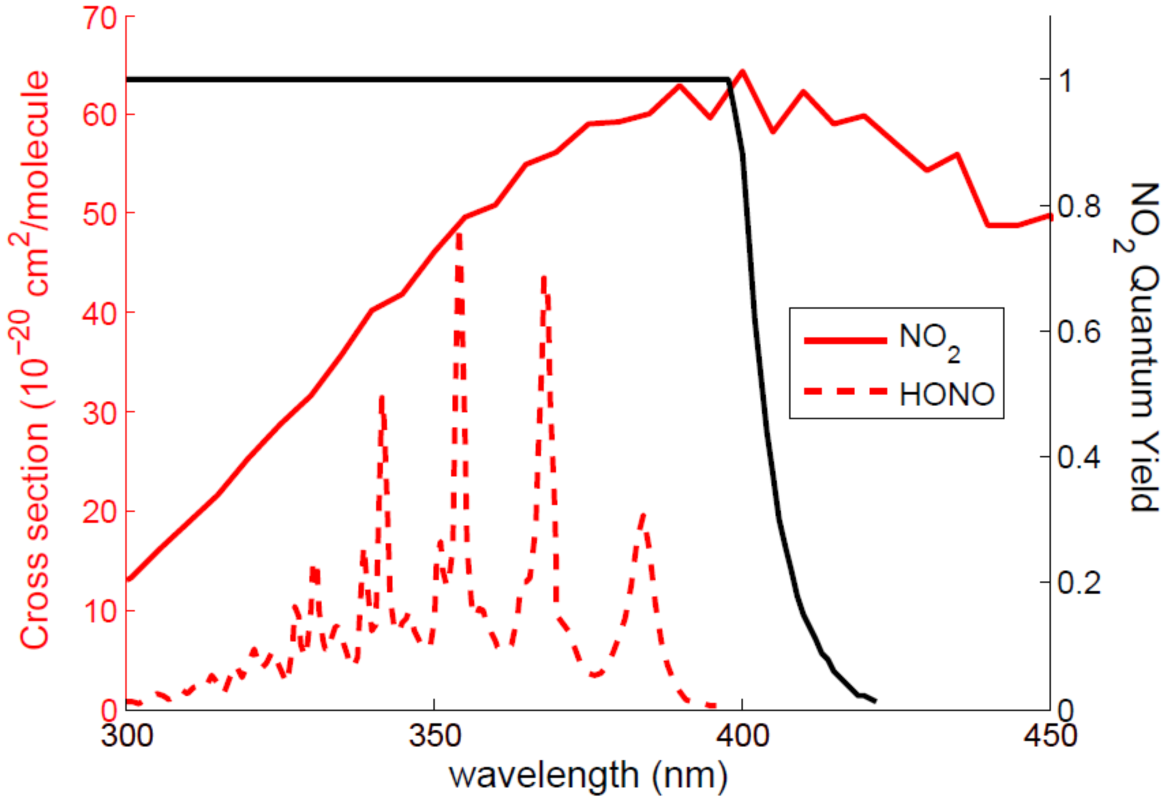




Data from Sander et al. (2006)

# Direct Optical Techniques

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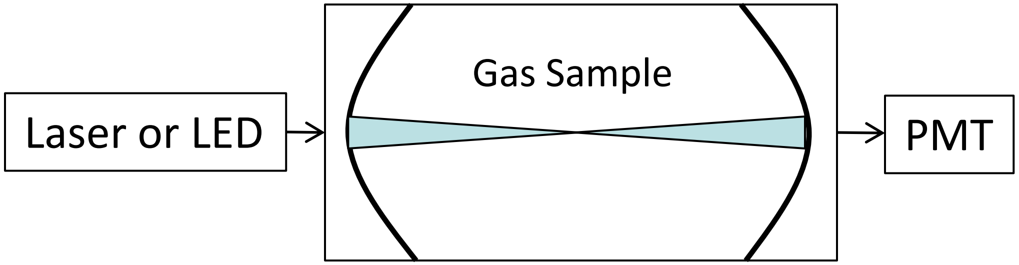
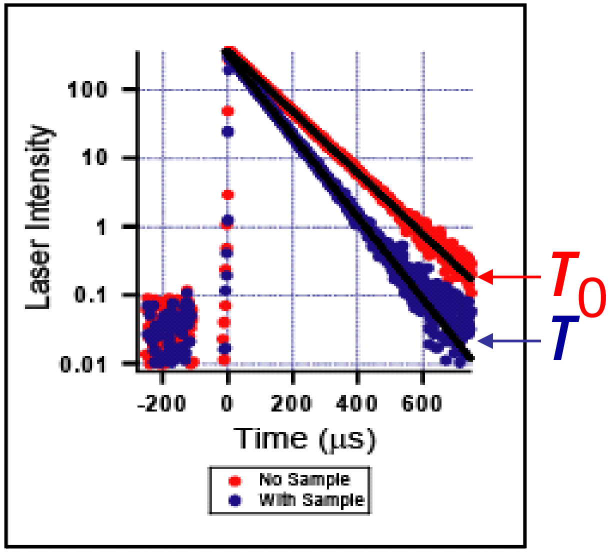
- Cavity ringdown spectroscopy
  - instrument manufactured by Los Gatos Research, Inc.




$$N(cm^{-3}) = \frac{1}{c\sigma}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$




- 10 s time resolution
- Advantage → DIRECT measurement
- Disadvantages → not-necessarily specific to $NO_2$, but to any molecule that absorbs light at 405 nm

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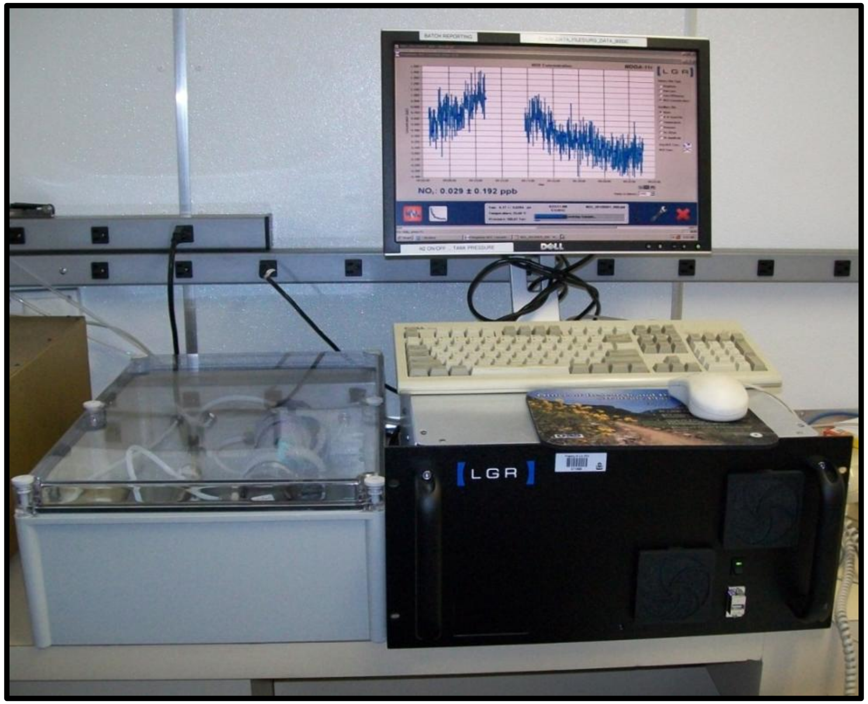


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# Direct Optical Techniques

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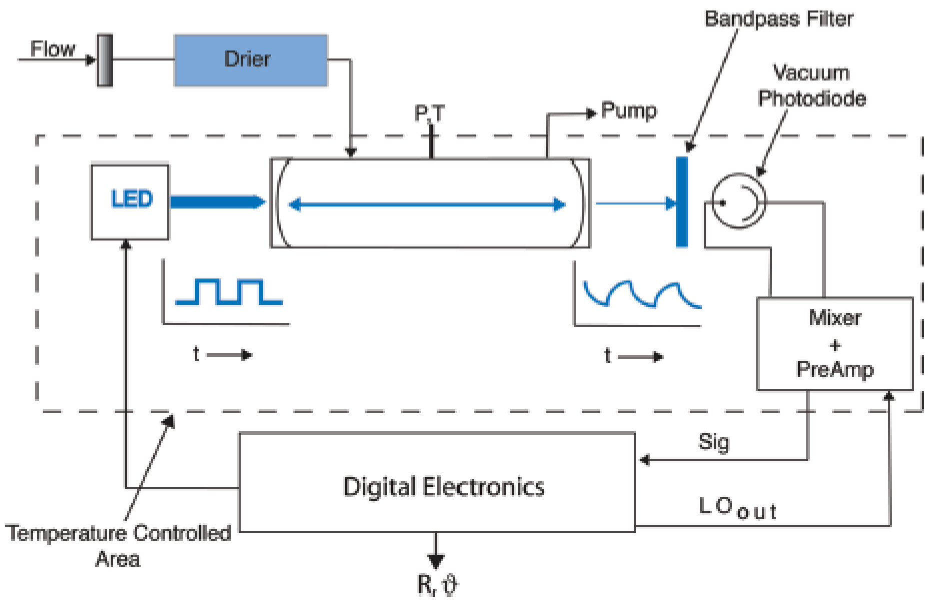


- Advantage → DIRECT measurement
- Disadvantage → not-necessarily specific to $NO_2$, but to any molecule that absorbs light at ~450 nm
- 2 versions: fast response (1 s) and ambient (10 s)



Kebabian et al. ES&T 2008

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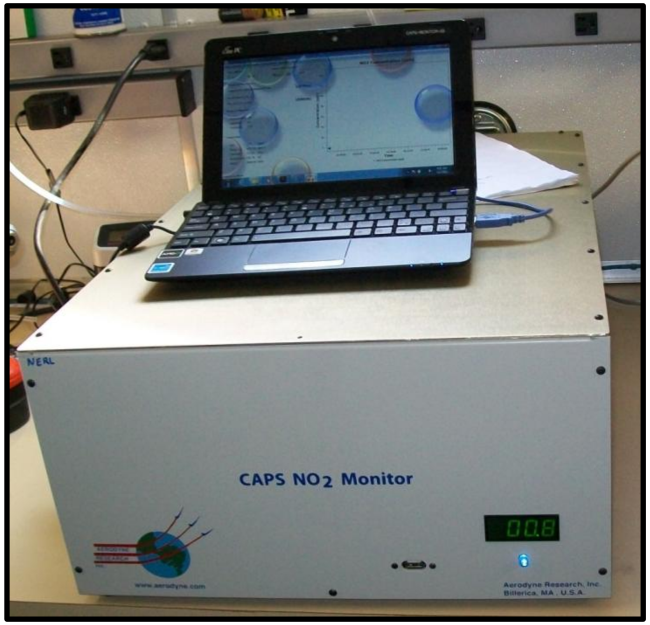


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- 2 versions: fast response (1 s) and ambient (10 s)

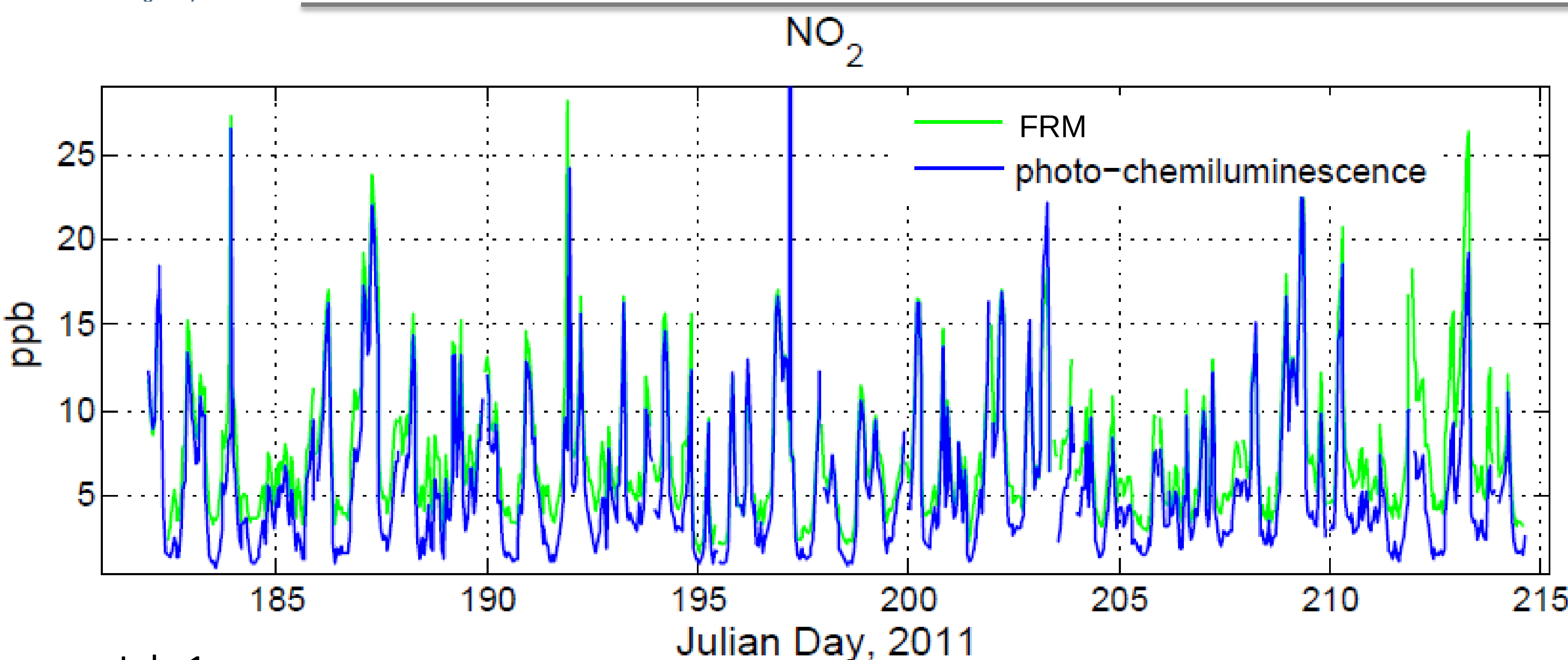
# NASA DISCOVER-AQ and EPA collaboration

• Supplement the existing local monitoring sites with $NO_2$ measurement technologies → satellite validation.

• First deployment was July 2011 in/around the greater Baltimore/DC metro area.

• Deployed two $NO_x$ monitors: one FRM and one photolytic-chemiluminescence

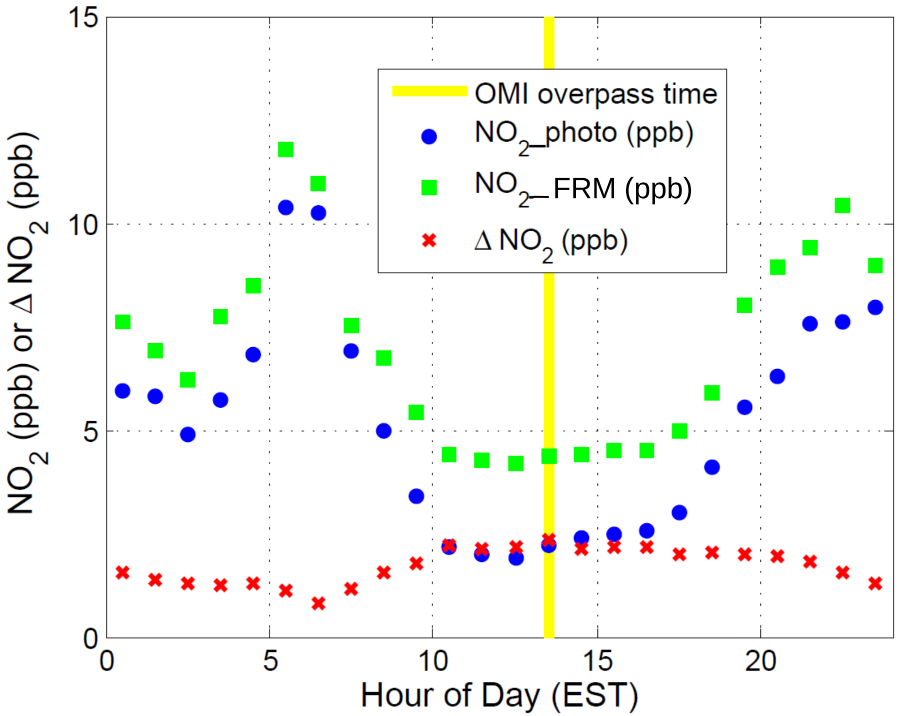
# Results from Padonia, MD Ground Site




July 1

Aug 2

# Preliminary Results from Padonia, MD Ground Site




$$\Delta NO_2 = NO_2\_FRM - NO_2\_photo$$

- The interference in the FRM monitor over predicts by ~50% during the hours surrounding noon.

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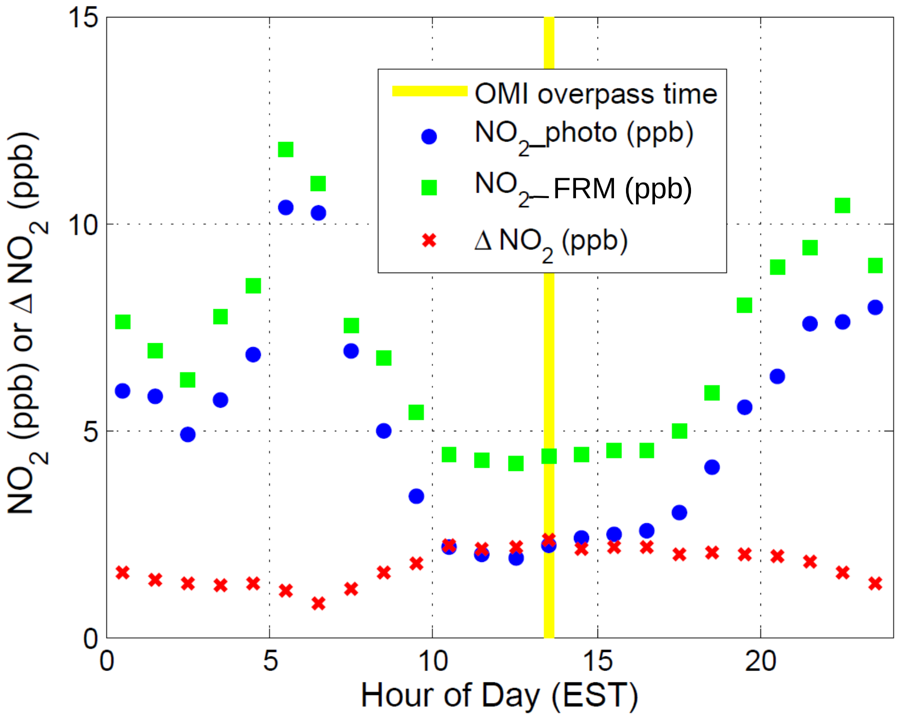


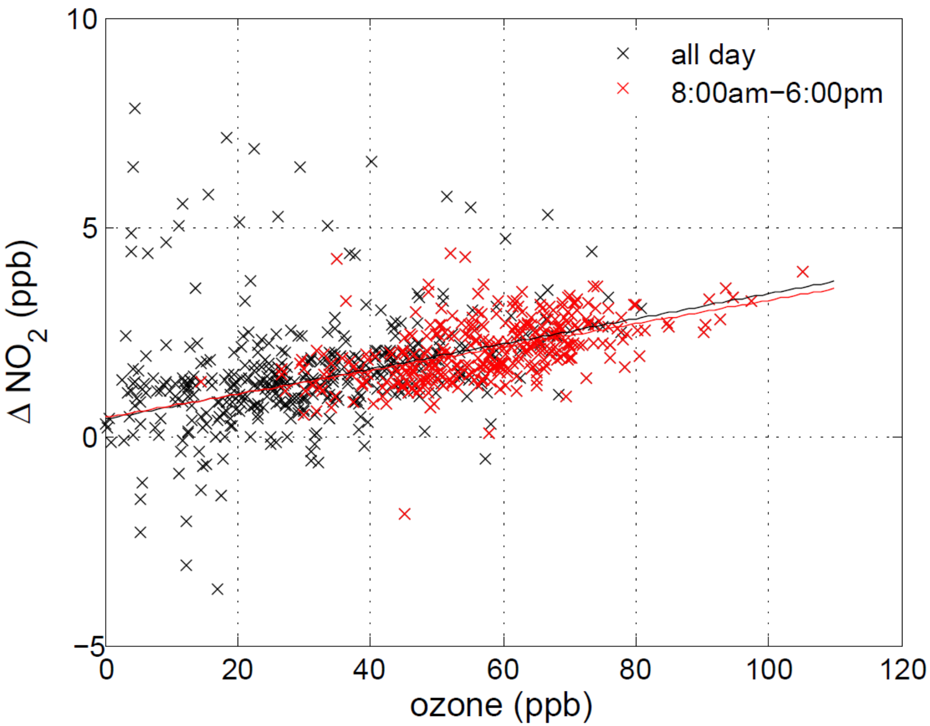


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# EPA's AIRS site, RTP, NC

EPA United States Environmental Protection Agency

- Currently conducting an intercomparison of direct optical, photolytic conversion, and FRM monitors throughout the summer months.

- Site operational with all monitors starting in mid – February 2012.

- Glass inlet, 5 m AGL, all instruments sample from common sampling manifold.

# Monitors Tested

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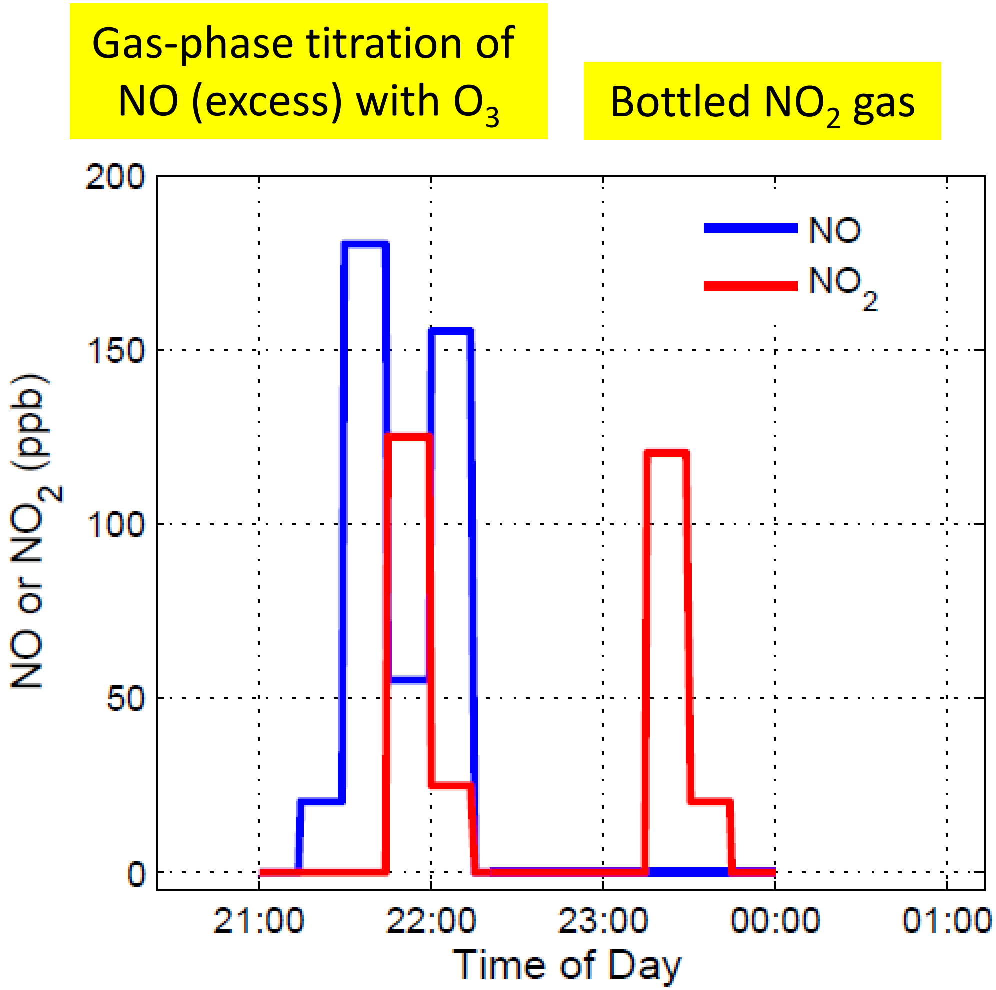
Agency

| ***Manufacturer and Model*** | ***Operation Principle*** | ***FRM/FEM status*** |
|---|---|---|
| Teledyne T200U | Moly-chemiluminescence | FRM |
| Teledyne 200EUP | Photolytic-chemiluminescence | FEM (application approved, designation imminent) |
| Aerodyne CAPS (both versions: fast response and ambient) | Cavity attenuated phase shift | -- |
| Los Gatos Research CRDS | Cavity ringdown spectroscopy | -- |

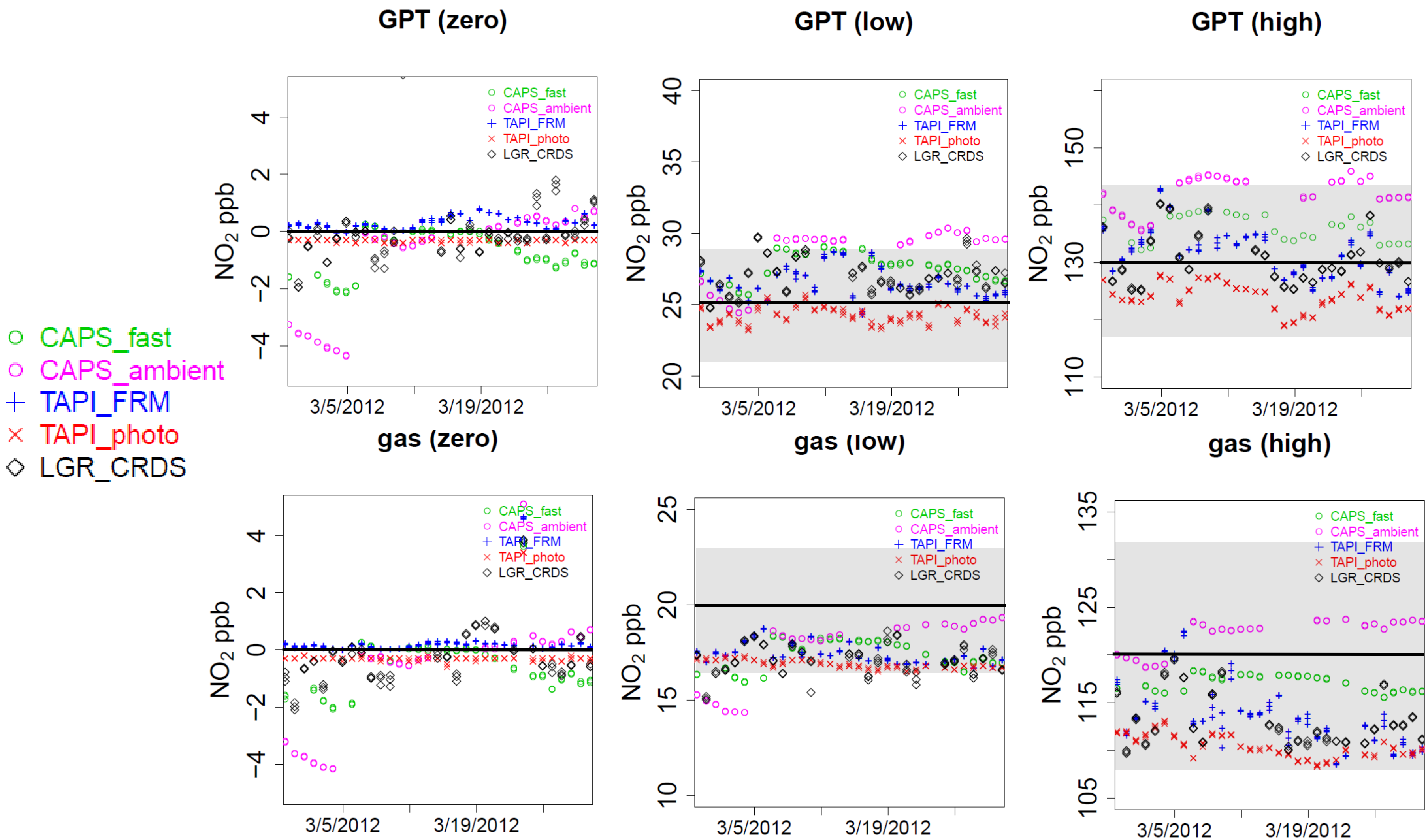
# Instrument Specifics

| ***Manufacturer and Model*** | ***Size (h x w x l)*** | ***weight (lbs.)*** | ***Power (W)*** | ***Sample flow, vol (Lpm)*** | ***Cost ($USD)*** |
|---|---|---|---|---|---|
| Teledyne T200U | 7”x 17”x 24” | 55 | 500 | 1.0 | ~16K |
| Teledyne 200EUP | 7”x 17”x 24” | 61 | 600 | 1.1 | ~25K |
| Aerodyne CAPS (both versions: fast response and ambient) | 9”x 17”x 26” | 27 | <100 | 0.9 (ambient) 4.5 (fast) | ~25K |
| Los Gatos Research CRDS | 7”x 19”x 24” (plus external drier) | 60 | 100 | 0.9 | ~30K |

# Nightly span/zero cycle



# March 2012 Span/Zero checks

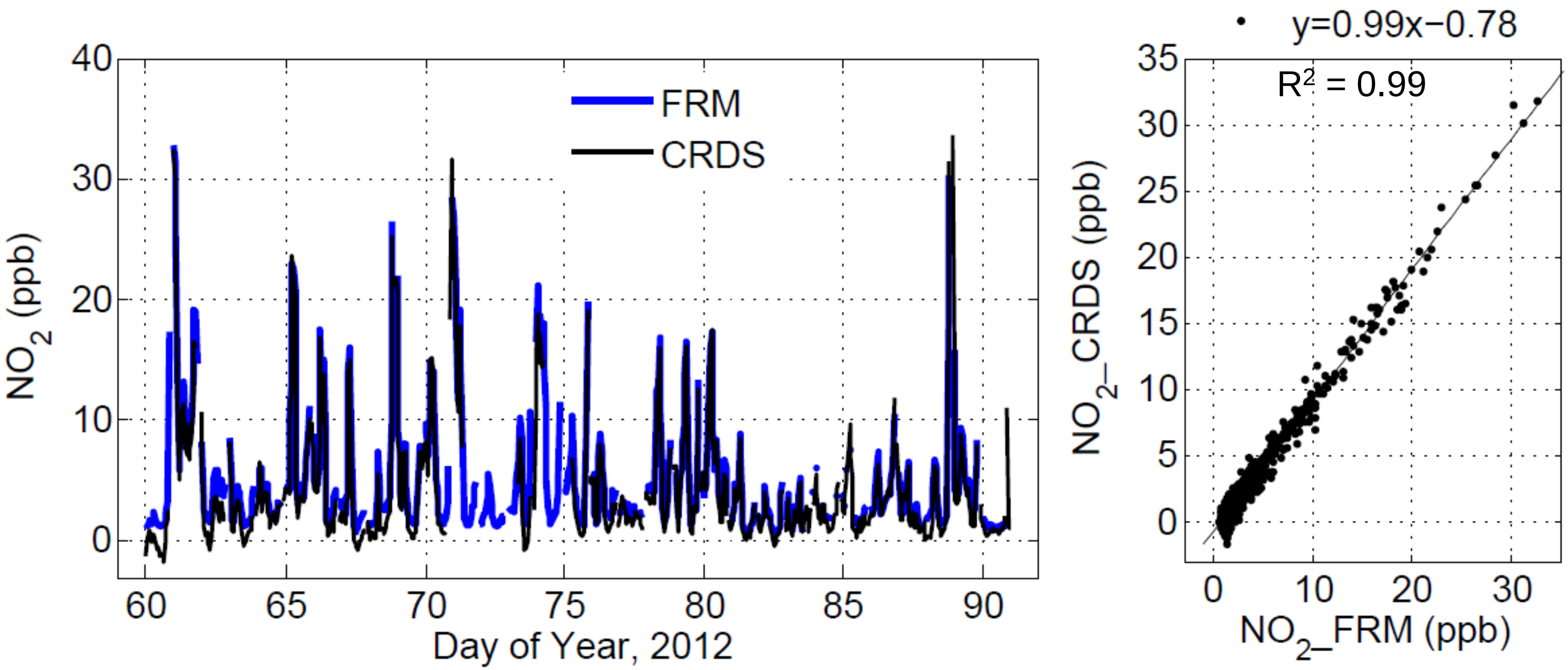





- Instruments within 15% of low span check and within 10% of high span check.

# Initial Performance Characterization

- EPA's AIRS site – RTP, NC; March 2012



# Operational Experiences

| *Manufacturer and Model* | *Data Interface/Accessibility* | *Calibration Procedures* |
|---|---|---|
| Teledyne T200U | - easily interfaced to our Envidas Ultimate data logger | - zero, high NO span to set slope and offset |
| Teledyne 200EUP | | - zero, high NO span to set slope and offset; then determine conversion efficiency using $NO_2$ |
| Aerodyne CAPS (both versions: fast response and ambient) | - Currently not interfaced with our data logger; operates using Aerodyne software which generates .txt files (comma delimited) | - Multipoint calibration periodically suggested to compare with factory calibration. Manual baseline check required weekly. |
| Los Gatos Research CRDS | - Can be interfaced with data logger via the provided 0-5V analog out signal; however no 'status' flag provided (yet); using .txt files generated by the instrument (tab delimited) | - Automatically checks the baseline signal at user defined interval; no further calibration required. |

# $NO_2$ Research Initiatives and Next Steps

United States Environmental Protection Agency

**ORD's Current Initiatives for $NO_2$ (FY12- FY15) include:**

- Method inter-comparison through the summer
    - Including detailed $NO_y$ and reduced nitrogen speciation to look at potential interferences
- Develop calibration procedures for direct measurement techniques
    - $NO_2$ cylinder vs GPT
- Detailed laboratory based assessments
    - Interference testing
    - 40 CFR part 53 subpart B performance testing
- Develop and document performance criteria including calibration and challenge procedures
- Evaluate optical monitors in a near-roadway environment

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